

Title: AMINO ALKYLPHENOL EMULSIFIERS FOR AN AQUEOUS
HYDROCARBON FUEL

This is a continuation in part of U.S. Application No. 09/483,481 filed January 14, 2000, which is a continuation in part of U.S. Application No. 09/390,925 filed September 7, 1999, which is a continuation in part of U.S. Application No. 09/349,268 filed July 7, 1999, and a continuation in part of U.S. Application No. 09/755,577 filed January 5, 2001. All of the disclosures in the prior applications are incorporated herein by reference in their entirety.

Field of the Invention

The invention relates to an amino alkylphenol emulsifier that is the reaction product of an alkylphenol, an aldehyde and an amine. More particularly, the invention relates to novel amino alkylphenol emulsifiers that are used for making an aqueous hydrocarbon fuel suitable for combustion in engines.

Background of the Invention

Internal combustion engines, in particular, diesel fueled engines produce NO_x due to the relatively high flame temperatures reached during combustion. Nitrogen oxides are an environmental issue because they contribute to smog and pollution. Governmental regulation and environmental concerns have driven the need to reduce NO_x emissions from engines. The reduction of NO_x production includes the use of catalytic converters, using "clean" fuels, recirculation of exhaust and engine timing changes. These methods are typically expensive or complicated to be commercially used.

Internal combustion engines, especially diesel engines, using water mixed with fuel in the combustion chamber can produce lower NO_x, hydrocarbon and particulate emissions per unit of power output. Water does not combust but lowers the peak combustion temperature resulting in reduced particulates and NO_x formation. When water is added to the fuel it forms an emulsion and these emulsions are generally unstable. Stable water fuel emulsions of small particle size are difficult to reach and maintain. It would be advantageous to provide a stable water in fuel emulsion that is stable in storage.

It has been found advantageous to produce a stable water in fuel emulsion by employing a novel amino alkylphenol emulsifier that is the reaction product of an alkylphenol, an aldehyde and an amine.

The term "NOx" is used herein to refer to any of the nitrogen oxides, NO, NO₂, N₂O, or mixtures of two or more thereof. The terms "aqueous hydrocarbon fuel emulsion" and "water fuel emulsion" are interchangeable. The terms "aqueous hydrocarbon fuel" and "water fuel blend" are interchangeable.

Summary of the Invention

The invention relates to an emulsifier to make an aqueous hydrocarbon fuel emulsion comprised of water, fuel such as diesel, gasoline or the like and an emulsifier. The emulsifier includes but is not limited to

(i) at least one fuel-soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl substituent of said acylating agent having about 50 to about 500 carbon atoms;

(ii) at least one of an ionic or a nonionic compound having a hydrophilic-lipophilic balance (HLB) of about 1 to about 40;

(iii) mixture of (ii) with (i); and

(iv) a water-soluble compound selected from the group consisting of amine salts, ammonium salts, azide compounds, nitrate esters, nitramine, nitrocompounds, alkali metal salts, alkaline earth metal salts, in combination with (i), (ii), (iii) or (v) or (vii);

(v) the reaction product of polyacidic polymer with at least one fuel soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia, an amine or a polyamine;

(vi) an amino alkylphenol which is made by reacting an alkylphenol, an aldehyde and an amine resulting in an amino alkylphenol, and

(vii) the combination of (vi) with (i), (ii), (iii), (iv), (v) and combinations thereof.

The invention further relates to a process for making an aqueous hydrocarbon fuel composition comprising:

a) mixing a liquid hydrocarbon fuel and at least one emulsifier to form a hydrocarbon fuel emulsifier mixture wherein the emulsifier comprises an amino alkylphenol which is the reaction product of an alkylphenol, an aldehyde and an amine; and

b) mixing the hydrocarbon fuel emulsifier mixture with water or water and ammonium nitrate under emulsification conditions to form an aqueous hydrocarbon fuel composition, wherein the aqueous hydrocarbon fuel composition includes a discontinuous

phase, the discontinuous aqueous phase being comprised of aqueous droplets having a mean diameter of 1.0 micron or less.

The invention further relates to an aqueous hydrocarbon fuel composition comprising:

- a) a continuous phase of hydrocarbon fuel,
- b) a discontinuous aqueous phase being comprised of aqueous droplets having a mean diameter of 1.0 micron or less and
- c) an emulsifying amount of an emulsifier composition comprising an amino alkylphenol which is the reaction product of an alkyl phenol, an aldehyde, and an amine.

The Water Fuel Emulsions

The invention provides for a batch, semi-batch or continuous process for making an aqueous hydrocarbon fuel by forming a stable emulsion in which the water is suspended in a continuous phase of fuel and wherein the water droplets have a mean diameter of 1.0 microns or less. The water fuel emulsions are comprised of: a continuous fuel phase; a discontinuous water or aqueous phase; and an emulsifying amount of an emulsifier. The emulsions may contain other additives that include but are not limited to cetane improvers, organic solvents, antifreeze agents, and the like. The water or aqueous phase of the aqueous hydrocarbon fuel emulsion is comprised of droplets having a mean diameter of 1.0 micron or less. Thus, the emulsification generally occurs by shear mixing and is conducted under sufficient conditions to provide such a droplet size.

The process is generally occurs under ambient conditions at atmospheric pressure. The process generally occurs at ambient temperature. In one embodiment the temperature is in the range of about ambient temperature to about 212°F, and in another embodiment in the range of about 40°F to about 150°F.

These emulsions may be prepared by the steps of (1) mixing the fuel, emulsifier and other desired additives using standard mixing techniques to form a fuel-chemical additives mixture and (2) mixing the fuel-chemical additives mixture with water and optionally an antifreeze agent under emulsification conditions to form the desired aqueous hydrocarbon fuel emulsion. Alternatively, the water-soluble compounds used in the emulsifier can be mixed with the water prior to the emulsification.

Optionally, additives may be added to the emulsifier, the fuel, the water or

combinations thereof. The additives include but are not limited to cetane improvers, organic solvents, antifreeze agents, surfactants, other additives known for their use in fuel and the like. The additives are added to the emulsifier, hydrocarbon fuel or the water prior to and in the alternative at the emulsification step depending upon the solubility of the additive.

5 However, it is preferable to add the additives to the emulsifier to form an additive emulsifier mixture. The additives are generally in the range of about 1% to about 40% by weight, in another embodiment about 5% to about 30% by weight, and in another embodiment about 7% to about 25% by weight of the additive emulsifier mixture.

10 The water can include but is not limited to antifreeze, ammonium nitrate or mixtures thereof. Ammonium nitrate is generally added to the water mixture as an aqueous solution. In one embodiment the water, the alcohol and/or the ammonium nitrate are mixed dynamically and fed continuously to the fuel additives stream. In another embodiment the water, antifreeze, ammonium nitrate or mixtures thereof flow out of separate tanks and/or combinations thereof into or mixed prior to the emulsification. In one embodiment the water, 15 water alcohol, water-ammonium-nitrate, or water-alcohol ammonium nitrate mixture meets the hydrocarbon fuel additives mixture immediately prior to or in the emulsification step.

The hydrocarbon fuel/additive mixture contains about 50% to about 99% by weight, in another embodiment about 85% to about 98% by weight, and in another embodiment about 95% to about 98% by weight hydrocarbon fuel, and it further contains about 0.05% to about 20 25%, in another embodiment about 1% to about 15%, and in another embodiment about 1% to about 5% by weight of the emulsifier.

High-shear devices that may be used include but are not limited to IKA Work Dispax, the IK shear mixers include the DR3-6 with three stages of rotor/stator combinations. The tip speed of the rotor/stator generators may be varied by a variable frequency drive that controls 25 the motor. The Silverson mixer is a two-stage mixer, which incorporates a rotor/stator design. The mixer has high-volume pumping characteristics similar to centrifugal pump. Inline shear mixers by Silverson Corporation (a rotor-stator emulsification approach); Jet Mixers (venturi-style/cavitation shear mixers), Ultrasonolator made by the Sonic Corp. (ultrasonic emulsification approach), Microfluidizer shear mixers available by Microfluidics 30 Inc. (high-pressure homogenization shear mixers), ultrasonic mixers, and any other available high-shear mixer.

A programmable logic controller (plc), may be provided for governing the flow of the aqueous hydrocarbon fuel additive mixture, the water, and aqueous hydrocarbon fuel emulsion thereby controlling the flow rates and mixing ratio in accordance with the prescribed blending rates. The plc stores component percentages input by the operator. The plc then uses these percentages to define volumes/flow of each component required. Continuous flow sequence is programmed into the plc. The plc electronically monitors all level switches, valve positions and fluid meters.

The Liquid Hydrocarbon Fuel

The liquid hydrocarbon fuel comprises hydrocarbonaceous petroleum distillate fuel, non-hydrocarbonaceous water, oils, liquid fuels derived from vegetables, liquid fuels derived from mineral and mixtures thereof. The liquid hydrocarbon fuel may be any and all hydrocarbonaceous petroleum distillate fuels including not limited to motor gasoline as defined by ASTM Specification D439 or diesel fuel or fuel oil as defined by ASTM Specification D396 or the like (kerosene, naphtha, aliphatics and paraffinics). The liquid hydrocarbon fuels comprising non-hydrocarbonaceous materials include but are not limited to alcohols such as methanol, ethanol and the like, ethers such as diethyl ether, methyl ethyl ether and the like, organo-nitro compounds and the like; liquid fuels derived from vegetable or mineral sources such as corn, alfalfa, shale, coal and the like. The liquid hydrocarbon fuels also include mixtures of one or more hydrocarbonaceous fuels and one or more non-hydrocarbonaceous materials. Examples of such mixtures are combinations of gasoline and ethanol and of diesel fuel and ether. In one embodiment, the liquid hydrocarbon fuel is any gasoline. Generally, gasoline is a mixture of hydrocarbons having an ASTM distillation range from about 60°C at the 10% distillation point to about 205°C at the 90% distillation point. In one embodiment, the gasoline is a chlorine-free or low-chlorine gasoline characterized by a chlorine content of no more than about 10 ppm.

In one embodiment, the liquid hydrocarbon fuel is any diesel fuel. Diesel fuels typically have a 90% point distillation temperature in the range of about 300°C to about 390°C, and in one embodiment about 330°C to about 350°C. The viscosity for these fuels typically ranges from about 1.3 to about 24 centistokes at 40°C. The diesel fuels can be classified as any of Grade Nos. 1-D, 2-D or 4-D as specified in ASTM D975. The diesel fuels may contain alcohols and esters. In one embodiment the diesel fuel has a sulfur content

of up to about 0.05% by weight (low-sulfur diesel fuel) as determined by the test method specified in ASTM D2622-87. In one embodiment, the diesel fuel is a chlorine-free or low-chlorine diesel fuel characterized by chlorine content of no more than about 10 ppm.

The liquid hydrocarbon fuel is present in the aqueous hydrocarbon fuel emulsion at a concentration of about 50% to about 95% by weight, and in one embodiment about 60% to about 95% by weight, and in one embodiment about 65% to about 85% by weight, and in one embodiment about 80% to about 90% by weight of the aqueous hydrocarbon fuel emulsion.

The Water

The water used in the aqueous hydrocarbon fuel emulsion may be taken from any source. The water includes but is not limited to tap, deionized, demineralized, purified, for example, using reverse osmosis or distillation, and the like.

The water may be present in the aqueous hydrocarbon fuel emulsions at a concentration of about 1% to about 50% by weight, and in one embodiment about 5% to about 50% by weight, and in one embodiment about 5% to about 40% by weight, and in one embodiment about 5% to about 25% by weight, and in one embodiment about 10% to about 20% water.

The Emulsifier

Fuel Soluble Product (i)

The fuel-soluble product (i) may be at least one fuel-soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl substituent of said acylating agent having about 50 to about 500 carbon atoms, and is described in greater detail in USSN 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein.

The hydrocarbyl-substituted carboxylic acid acylating agents may be carboxylic acids or reactive equivalents of such acids. The reactive equivalents may be acid halides, anhydrides, or esters, including partial esters and the like. The hydrocarbyl substituents for these carboxylic acid acylating agents may contain from about 50 to about 500 carbon atoms, and in one embodiment about 50 to about 300 carbon atoms, and in one embodiment about 60 to about 200 carbon atoms. In one embodiment, the hydrocarbyl substituents of these acylating agents have number average molecular weights of about 700 to about 3000, and in one embodiment about 900 to about 2300.

The hydrocarbyl-substituted carboxylic acid acylating agents may be made by reacting one or more alpha-beta olefinically unsaturated carboxylic acid reagents containing 2 to about 20 carbon atoms, exclusive of the carboxyl groups, with one or more olefin polymers as described more fully hereinafter.

5 In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent is a polyisobutene-substituted succinic anhydride, the polyisobutene substituent having a number average molecular weight of about 1,500 to about 3,000, in one embodiment about 1,800 to about 2,300, in one embodiment about 700 to about 1300, in one embodiment about 800 to about 1000, said first polyisobutene-substituted succinic anhydride being characterized by about 1.3 to about 2.5, and in one embodiment about 1.7 to about 2.1 In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent is a polyisobutene-substituted succinic anhydride, the polyisobutene substituent having a number average molecular weight of about 1,500 to about 3,000, and in one embodiment about 1,800 to about 2,300, said first polyisobutene-substituted succinic anhydride being characterized by about 1.3 to about 2.5, and in one embodiment about 1.7 to about 2.1, in one embodiment about 1.0 to about 1.3, and in one embodiment about 1.0 to about 1.2 succinic groups per equivalent weight of the polyisobutene substituent.

15 The fuel-soluble product (i) may be formed using ammonia, an amine and/or metals such as Na, K, Ca, and the like. The amines useful for reacting with the acylating agent to form the product (i) include monoamines, polyamines, and mixtures thereof and amines may be primary, 20 secondary or tertiary amines.

Examples of primary and secondary monoamines include ethylamine, diethylamine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyl laurylamine, oleylamine, N-methyloctylamine, dodecylamine, and octadecylamine. Suitable examples of tertiary monoamines include trimethylamine, triethylamine, tripropylamine, 25 tributylamine, monoethyldimethylamine, dimethylpropylamine, dimethylbutylamine, dimethylpentylamine, dimethylhexylamine, dimethylheptylamine, and dimethyloctylamine. The amines include but are not limited to hydroxyamine, mono-, di-, and triethanolamine, dimethylethanol amine, diethylethanol amine, di-(3-hydroxy propyl) amine, N-(3-hydroxybutyl) amine, N-(4-hydroxy butyl) amine, and N,N-di-(2-hydroxypropyl) amine; alkylene polyamines 30 such as methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, and the like. Specific examples of such polyamines include

ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, trimethylene diamine, tripropylene tetramine, tetraethylene pentamine, hexaethylene heptamine, pentaethylene hexamine, or a mixture of two or more thereof; ethylene polyamine; is a polyamine bottoms or a heavy polyamine. The fuel-soluble product (i) may be a salt, an ester, an ester/salt, an amide, an imide, or a combination of two or more thereof.

The fuel-soluble product (i) may be present in the water-fuel emulsion at a concentration of up to about 15% by weight based on the overall weight of the emulsion, and in one embodiment about 0.1 to about 15% by weight, and an one embodiment about 0.1 to about 10% by weight, and in one embodiment about 0.1 to about 5% by weight, and in one embodiment about 0.1 to about 2% by weight, and in one embodiment about 0.1 to about 1% by weight, and in one embodiment about 0.1 to about 0.7% by weight.

The Ionic or Nonionic Compound (ii)

The ionic or nonionic compound (ii) has a hydrophilic-lipophilic balance (HLB, which refers to the size and strength of the polar (hydrophilic) and non-polar (lipophilic) groups on the surfactant molecule) in the range of about 1 to about 40, and in one embodiment about 4 to about 15 and is described in greater detail in USSN 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein. Examples of these compounds are disclosed in McCutcheon's Emulsifiers and Detergents, 1998, North American & International Edition. Pages 1-235 of the North American Edition and pages 1-199 of the International Edition are incorporated herein by reference for their disclosure of such ionic and nonionic compounds having an HLB in the range of about 1 to about 40, in one embodiment about 1 to about 30, in one embodiment about 1 to 20, and in another embodiment about 1 to about 10. Useful compounds include alkanolamides, carboxylates including amine salts, metallic salts and the like, alkylarylsulfonates, amine oxides, poly(oxyalkylene) compounds, including block copolymers comprising alkylene oxide repeat units, carboxylated alcohol ethoxylates, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines and amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, fatty acid amides, including but not limited to amides from tall oil fatty acids and polyamides (3066), glycerol esters, glycol esters, sorbitan esters, imidazoline derivatives, lecithin and derivatives, lignin and derivatives, monoglycerides and derivatives, olefin sulfonates, phosphate esters and derivatives, propoxylated and ethoxylated fatty acids or alcohols or alkylphenols, sorbitan derivatives, sucrose esters and derivatives, sulfates or alcohols

or ethoxylated alcohols or fatty esters, sulfonates of dodecyl and tridecyl benzenes or condensed naphthalenes or petroleum, sulfosuccinates and derivatives, and tridecyl and dodecyl benzene sulfonic acids.

Emulsifier Mixture (iii)

A mixture of (i) and (ii) is described in greater detail in USSN 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein.

The Water-Soluble Compound (iv)

The water-soluble compound may be an amine salt, ammonium salt, azide compound, nitro compound, alkali metal salt, alkaline earth metal salt, or mixtures of two or more thereof and is described in greater detail in USSN 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein. These compounds are distinct from the fuel-soluble product (i) and the ionic or nonionic compound (ii) discussed above. These water-soluble compounds include organic amine nitrates, nitrate esters, azides, nitramines and nitro compounds. Also included are alkali and alkaline earth metal carbonates, sulfates, sulfides, sulfonates, and the like.

Particularly useful are the amine or ammonium salts ammonium nitrate, ammonium acetate, methylammonium nitrate, methylammonium acetate, ethylene diamine diacetate, urea nitrate, urea, guanidinium nitrate and the like.

The water-soluble compound may be present in the water-fuel emulsion at a concentration of about 0.001 to about 1% by weight, and in one embodiment from about 0.01 to about 1% by weight.

Emulsifier (v)

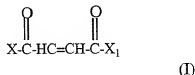
In one embodiment the emulsifier (v) is the reaction product of A) a polyacidic polymer, B) at least one fuel soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent, and C) a hydroxy amine and/or a polyamine and is described in greater detail in in USSN 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein.

The fuel soluble product is made by reacting at least one hydrocarbyl-substituted carboxylic agent with a hydroxy amine and/or polyamine and is described earlier in the specification.

The polyacidic polymers used in the reaction include but are not limited to C₄ to C₃₀, preferably C₈ to C₂₀ olefin/maleic anhydride copolymers. The alpha-olefins include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-eicosene, 1-docosene, 1-triacontene, and the like. the alpha olefin fractions that are useful include C₁₅₋₁₈ alpha-olefins, C₁₂₋₁₆ alpha-olefins, C₁₄₋₁₆ alpha-olefins, C₁₄₋₁₈ alpha-olefins, C₁₆₋₁₈ alpha-olefins, C₁₈₋₂₄ alpha-olefins, C₁₈₋₃₀ alpha-olefins, and the like. Mixtures of two or more of any of the foregoing alpha-olefins or alpha-olefin fractions may be used.

Other polyacidic polymers suitable for reaction include but are not limited to maleic anhydride/styrene copolymers; poly-maleic anhydride; acrylic and methacrylic acid containing polymers; poly-(alkyl)acrylates; reaction products of maleic anhydride with polymers with multiple double bonds; and combinations thereof. The preferred is polyacidic polymer C₁₈ [1-octadecene]/maleic anhydride copolymer.

In another embodiment the polyacidic polymer is a copolymer of an olefin and a monomer having the structure:



wherein X and X₁ are the same or different provided that at least one of X and X₁ is such that the copolymer can function as a carboxylic acylating agent.

The olefin includes a polymerizable olefin characterized by the presence of one or more ethylenically unsaturated groups. The olefin monomers include but are not limited to 1-hexene, octadecene-1 and diisobutylene. The olefin preferably is a C₄-C₃₀ olefin.

The emulsifier produced from the reaction product of the polyacidic polymer with the fuel soluble product (i) comprises about 25% to about 95% of fuel soluble product and about 0.1% to about 50% of the polyacidic polymer; preferably about 50% to about 92% fuel soluble product and about 1% to about 20% of the polyacidic polymer, and most preferably about 70% to about 90% of fuel soluble product and about 5% to about 10% of the polyacidic polymer. In one embodiment the emulsifier is described as a polyalkenyl succinimide crosslinked with an olefin/maleic anhydride copolymer.

Amino Alkylphenol Emulsifier (vi) and (vii)

The amino alkyl emulsifier is comprised of the reaction product of an amino alkylphenol, an aldehyde, and an amine resulting in amino alkylphenol. The amino alkylphenol can be made by (a) the reaction of alkylphenol directly with an aldehyde and an amine resulting in an alkylphenol monomer connected by a methylene group to an amine, (b) the reaction of an alkylphenol with an aldehyde resulting in an oligomer wherein the alkylphenols are bridged with methylene groups, the oligomer is then reacted with more aldehyde and an amine to give a Mannich product, or (c) a mixture of (a) and (b)

The alkylphenols have an alkyl group selected from C₁ to C₂₀₀, preferably C₆ to C₁₇₀ wherein the alkyl group is either linear, branched or a combination thereof. The alkylphenols include, but are not limited to, polypropylphenol, polybutylphenol, poly(isobutenyl)phenol, polyamylphenol, tetrapropylphenol, similarly substituted phenols and the like. The preferred alkylphenols are tetrapropenylphenol and poly(isobutenyl)phenol. For example, in place of the phenol, alkyl-substituted compounds of resorcinol, hydroquinone, catechol, cresol, xlenol, amyl phenol, hydroxydiphenyl, benzylphenol, phenylethylphenol, methylhydroxydiphenyl, alpha and beta naphthol, alpha and beta methyl naphthol, tolynaphthol, xylynaphthol, benzlnaphthol, anthranol, phenylmethylnaphthol, phenanthrol, monomethyl ether of catechol, phenoxyphenol, chlorophenol, hydroxyphenyl sulfides and the like may be used.

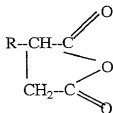
The aldehydes include, but are not limited to, aliphatic aldehydes, such as formaldehyde; acetaldehyde; aldol (β -hydroxy butyraldehyde); aromatic aldehydes, such as benzaldehyde; heterocyclic aldehydes, such as furfural, and the like. The aldehyde may contain a substituent group such as hydroxyl, halogen, nitro and the like; in which the substituent does not take a major part in the reaction. The preferred aldehyde is formaldehyde.

The amines are those which contain an amino group characterized by the presence of at least one active hydrogen atom. The amines may be primary amino groups, secondary amino groups, or combinations of primary and secondary amino groups.

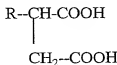
The amines include, but are not limited to, alkanoloamines such as monoethanol amine, diethanolamine, N-(2-aminoethyl) ethanolamine and the like; di- and polyamine (polyalkylene amines) such as dimethylaminopropylamine, 3-aminopropyl morpholine,

ethylenediamine, diethylenetriamine, triethylene tetramine, tetraethylene pentamine and the like including distillation bottoms such as HPAX (commercially available from The Union Carbide Corporation), E-100 (commercially available from Dow Chemical Co.), and the like; polyalkyl polyamines; propylenediamine, the aromatic amines such as o-, m- and p-phenylene diamine, diamino naphthalenes; the acid-substituted polyalkylpolyamines, such as N-acetyl tetraethylenepentamine, and the corresponding formyl-, propionyl-, butyryl-, and the like N-substituted compounds; and the corresponding cyclized compounds formed therefrom, such as the N-alkyl amines of imidazolidine and pyrimidine. (Secondary heterocyclic amines that are suitable are those characterized by attachment of a hydrogen atom to a nitrogen atom in the heterocyclic group such as morpholine, thiomorpholine, pyrrole, pyrroline, pyrrolidine, indole, pyrazole, pyrazoline, pyrazolidine, imidazole, imidazoline, imidazolidine, piperidine, phenoxazine, phenthiazine and their substituted analogs. Substituent groups attached to the carbon atoms of these amines are typified by alkyl, aryl, alkaryl, aralkyl, cycloalkyl, and amino compounds referred to above.)

The "amine" includes, but is not to be limited, to the product obtained by reacting an alkenyl succinic anhydride of the formula



or alkenyl succinic acid of the formula



with the amines of the foregoing paragraph.

In the above formulae, R is an alkylene group. The alkenyl radical can be straight-chain or branched-chain; and it can be saturated at the point of unsaturation by the addition of a substance that adds to olefinic double bonds, such as hydrogen, sulfur, bromine, chlorine, or iodine. There must be at least two carbon atoms in the alkenyl radical, but there is no real

upper limit to the number of carbon atoms therein. The alkenyl succinic acid anhydrides and the alkenyl succinic acids are interchangeable for the purposes of the present invention. Nonlimiting examples of the alkenyl succinic acid anhydride component are ethenyl succinic acid anhydride; ethenyl succinic acid; ethyl succinic acid anhydride; propenyl succinic acid anhydride; sulfurized propenyl succinic acid anhydride; butenyl succinic acid; 2-methylbutenyl succinic acid anhydride; 1,2-dichloropentyl succinic acid anhydride; hexenyl succinic acid anhydride; hexyl succinic acid; sulfurized 3-methylpentyl succinic acid anhydride; 2,3-dimethylbutenyl succinic acid anhydride; 3,3-dimethylbutenyl succinic acid; 1,2-dibromo-2-ethylbutyl succinic acid; heptenyl succinic acid anhydride; 1,2-diiodooctyl succinic acid; octenyl succinic acid anhydride; diisobutenyl succinic acid anhydride; 2-methylheptenyl succinic acid anhydride; 4-ethylhexenyl succinic acid; 2-isopropylpentenyl succinic acid anhydride; nonenyl succinic acid anhydride; 2-propylhexenyl succinic acid anhydride; decenyl succinic acid; decenyl succinic acid anhydride; 5-methyl-2-isopropylhexenyl succinic acid anhydride; 1,2-dibromo-2-ethyloctenyl succinic acid anhydride; decyl succinic acid anhydride; undecenyl succinic acid anhydride; 1,2-dichloroundecyl succinic acid; 3-ethyl-2-t-butylpentenyl succinic acid anhydride; tetrapropenyl succinic acid anhydride; tetrapropenyl succinic acid; triisobutenyl succinic acid anhydride, 2-propyl-nonyl succinic acid anhydride, 3-butyloctenyl succinic acid anhydride; tridecenyl succinic acid anhydride; tetradecenyl succinic acid anhydride; hexadecenyl succinic acid anhydride; sulfurized octadecenyl succinic acid; octadecyl succinic acid anhydride; 1,2-dibromo-2-methylpentadecenyl succinic acid anhydride; 8-propylpentadecyl succinic acid anhydride; eicosenyl succinic acid anhydride; 1,2-dichloro-2-methylnonadecenyl succinic acid anhydride; 2-octylododecenyl succinic acid; 1,2-diiodotetracosenyl succinic acid anhydride; hexacosenyl succinic acid; hexacosenyl succinic acid anhydride; hentriacontenyl succinic acid anhydride and combinations thereof. In general, alkenyl succinic acid anhydrides having from about 8 to about 35, and preferably, from about 9 to about 18 carbon atoms in the alkenyl group. Methods for preparing the alkenyl succinic acid anhydrides are known to those familiar with the art, the most feasible method comprising the reaction of an olefin with maleic acid anhydride.

The reaction is prepared by any known method such as an emulsion, a solution, a suspension, a continuous additive bulk process or the like. The reaction is carried out under

conditions that provide for the formation of the desired product. The reaction temperature is in the range of about 40°C to about 200°C, preferably about 50°C to about 160°C, and more preferably about 60°C to about 150°C. The reaction may be carried out at elevated or reduced pressure, but is preferably carried out at atmospheric pressure. The reaction is generally
5 carried out over a period of time in the range of about 15 minutes to about 8 hours, preferably about 1 hour to about 6 hours, and more preferably about 2 hours to about 4 hours.

The amino alkylphenols emulsifier of this invention may be made by reacting the alkylphenol:aldehyde:amine in a ratio range of 1:1:0.1 molar to 1:2:2 molar, in one embodiment preferably 1:0.9:0.1 to 1:1.9:1.9, in one embodiment preferably 1:1.5:1.2 molar
10 to 1:1.9:1.8 molar, and in one embodiment preferably 1:0.8:0.3 to 1:1.5:0.7, resulting in the amino alkylphenol emulsifier.

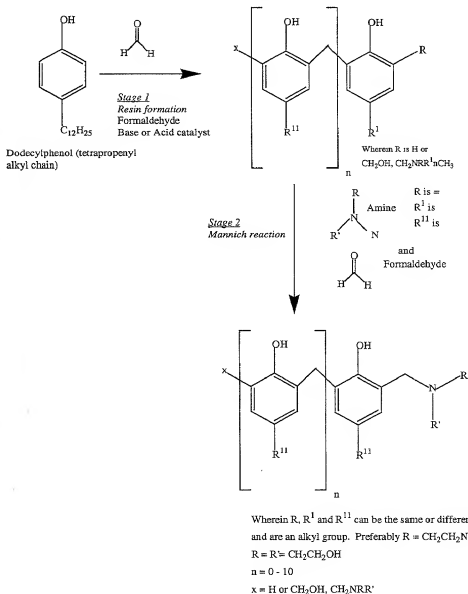
Ranges for the emulsifier treated in the water blend fuel are in the concentration of about 0.05% to about 20% by weight, and in another embodiment 0.05% to about 10% by weight, and in another embodiment about 0.1% to about 5%, and in another embodiment
15 0.1% to about 3% by weight of the total emulsion.

In an another embodiment of this invention the amino alkylphenol is made by the reaction of an alkylphenol with an aldehyde, resulting in an oligomer wherein the alkylphenols are bridged with methylene groups; then the oligomer is reacted with more aldehyde and amine to give the emulsifier Mannich product of this invention. The reaction is
20 prepared by any known method such as an emulsion, a solution, a suspension, a continuous addition bulk process. The reaction is carried out under conditions that provide for the formation of the desired product.

The reaction is carried out at a temperature in the range of about 0°C to about 150°C, preferably to about 20°C to about 100°C, and more preferably about 30°C to about 70°C over
25 a period of time in the range of about 15 minutes to about 8 hours, preferably about 1 hour to about 6 hours, and more preferably about 2.5 hours to about 5 hours, resulting in an oligomer wherein the alkylphenols are bridged with methylene groups. This intermediate product is then reacted in the range of about 1 mole oligomer:0.1 mole amine to about 1 mole oligomer:2 moles amine; preferably about 1 mole oligomer:0.2 mole amine to about 1 mole
30 oligomer:1.5 moles amines, and more preferably about 1 mole oligomer:0.3 moles amine to about 1 mole oligomer:0.9 moles amine, resulting in amino alkylphenol product.

This reaction occurs at a temperature of about 40°C to about 200°C, preferably about 50°C to about 160°C, and more preferably about 60°C to about 150°C. The reaction may be carried out at elevated to reduced pressure, but is preferably carried out at atmospheric pressure. The reaction continues until the Mannich product is formed.

5 This embodiment is illustrated as follows:



The emulsifier may be a mixture of the amine alkylphenol with

(i) at least one fuel-soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl substituent of said acylating agent having about 50 to about 500 carbon atoms;

(ii) at least one of an ionic or a nonionic compound having a hydrophilic-lipophilic balance (HLB) of about 1 to about 40;

(iii) mixture of (ii) with (i); and

(iv) a water-soluble compound selected from the group consisting of amine salts, ammonium salts, azide compounds, nitrate esters, nitramine, nitro compounds, alkali metal salts, alkaline earth metal salts, in combination with (i), (ii), (iii) or (v) or (vii);

(v) the reaction product of polyacidic polymer with at least one fuel soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia, an amine or a polyamine; and

(vi) combinations thereof.

The emulsifier may be present in the water fuel emulsion at a concentration of about 0.05% to about 20% by weight, in another embodiment about 0.05% to about 10% by weight, in another embodiment about 0.1% to about 5% by weight, and in a further embodiment of about 0.01% to about 3% by weight of the water fuel emulsion.

Cetane Improver

In one embodiment, the water-fuel emulsion contains a cetane improver. The cetane improvers that are useful include but are not limited to peroxides, nitrates, nitrites, nitrocarbamates, and the like. Useful cetane improvers include but are not limited to nitropropane, dinitropropane, tetranitromethane, 2-nitro-2-methyl-1-butanol, 2-methyl-2-nitro-1-propanol, and the like. Also included are nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols which may be monohydric or polyhydric. These include substituted and unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, and in one embodiment about 2 to about 10 carbon atoms. The alkyl group may be either linear or branched, or a mixture of linear or branched alkyl groups. Examples include methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, n-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, and isopropylcyclohexyl nitrate. Also useful are the nitrate esters of alkoxy-substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(2-ethoxy-ethoxy) ethyl nitrate, 1-methoxypropyl-2-

nitrate, 4-ethoxybutyl nitrate, etc., as well as diol nitrates such as 1,6-hexamethylene dinitrate. A useful cetane improver is 2-ethylhexyl nitrate.

The concentration of the cetane improver in the water-fuel emulsion may be at any concentration sufficient to provide the emulsion with the desired cetane number. In one embodiment, the concentration of the cetane improver is at a level of up to about 10% by weight, and in one embodiment about 0.05 to about 10% by weight, and in one embodiment about 0.05 to about 5% by weight, and in one embodiment about 0.05 to about 1% by weight.

Additional Additives

In addition to the foregoing materials, other fuel additives that are well known to those of skill in the art may be used in the water-fuel emulsions of the invention. These include but are not limited to dyes, rust inhibitors such as alkylated succinic acids and anhydrides, bacteriostatic agents, gum inhibitors, metal deactivators, upper cylinder lubricants, and the like.

The total concentration of chemical additives, including the foregoing emulsifiers, in the water-fuel emulsions of the invention may range from about 0.05 to about 30% by weight, and in one embodiment about 0.1 to about 20% by weight, and in one embodiment about 0.1 to about 15% by weight, and in one embodiment about 0.1 to about 10% by weight, and in one embodiment about 0.1 to about 5% by weight.

Organic Solvent

The additives, including the foregoing emulsifiers, may be diluted with a substantially inert, normally liquid organic solvent such as naphtha, benzene, toluene, xylene or diesel fuel to form an additive concentrate which is then mixed with the fuel and water to form the water-fuel emulsion.

The water-fuel emulsions may contain up to about 60% by weight organic solvent, and in one embodiment about 0.01 to about 50% by weight, and in one embodiment about 0.01 to about 20% by weight, and in one embodiment about 0.1 to about 5% by weight, and in one embodiment about 0.1 to about 3% by weight.

Antifreeze Agent

The water-fuel emulsions of the invention may additionally contain an antifreeze agent. The antifreeze agent is typically an alcohol. Examples include but are not limited to ethylene glycol, propylene glycol, methanol, ethanol, glycerol and mixtures of two or more thereof. The antifreeze agent is typically used at a concentration sufficient to prevent freezing of the water

used in the water-fuel emulsions. The concentration is therefore dependent upon the temperature at which the fuel is stored or used. In one embodiment, the concentration is at a level of up to about 20% by weight based on the weight of the water-fuel emulsion, and in one embodiment about 0.1 to about 20% by weight, and in one embodiment about 1 to about 10% by weight.

5 **The Engines**

The engines that may be operated in accordance with the invention include all compression-ignition (internal combustion) engines for both mobile (including marine) and stationary power plants including but not limited to diesel, gasoline, and the like. The engines that can be used include but are not limited to those used in automobiles, trucks such as all classes of truck, buses such as urban buses, locomotives, heavy duty diesel engines, stationary engines (how define) and the like. Included are on- and off-highway engines, including new engines as well as in-use engines. These include diesel engines of the two-stroke-per-cycle and four-stroke-per-cycle types.

15 **Specific Embodiments**

The following examples illustrate the invention. It should be understood, however, that that the invention is not limited to the specific details set forth in the examples.

General Procedures for Examples 1-22.

The formation of the amino alkylphenol by the oligomer reaction is as follows:

20 A base catalyst can be used in the resin formation, preferably alkali metal hydroxides such as potassium hydroxide, tetraalkylammonium hydroxides such as tetrabutylammonium hydroxide, and the like. An acid catalyst can be used in the resin formation, preferably an acid catalyst that is soluble in organic solvents, such as dodecylbenzenesulphonic acid. Catalysts can also be used in the Mannich reaction. Any source of the aldehyde can be used, 25 for instance if formaldehyde is used it can be formalin (formaldehyde solution in water), paraformaldehyde (paraform), or the like. Solvents can be used such as Caromax 26 (commercially available from Carless), Solvesso 150 (commercially available from Esso), kerosene, toluene, xylene, and the like.

30 In examples 1-22, two types of oligomer are made before the Mannich reaction with an amine. These are Resoles, where an excess of formaldehyde is used with respect to the alkylphenol and a basic catalyst is employed, and Novalaks where an excess of alkylphenol is

used with respect to the formaldehyde and an acidic catalyst is employed. The former oligomers tend to be of a lower molecular weight and contain residual methylol (CH_2OH) groups, whereas the latter tend to be of a higher molecular weight and contain no residual methylol groups.

- 5 The ratios of ingredients are as follows:

Molar ratio of ingredients	Catalyst (KOH or Bu_4NOH or dodecyl benzene sulphonic acid)	p-Dodecylphenol (tetrapropenyl derived)	Formaldehyde	Amine
Minimum	0.01	1	0.65 (Nov.) 1.0 (Res.)	0.4 (Res.), 0.2 (Nov.)
Optimum	0.01	12	1.35 (Res.) 0.8 (Nov.)	0.86 (Res.) 0.3 (Nov.)
Maximum	0.01	1	2 (Res.) 1.0 (Nov.)	2.0 (Res.) 0.4 (Nov.)

Res. = Resole
Nov. = Novalak

General Screening Procedure

For Examples 1-22, Emulsifier 1, was the coupled, reaction product of 2 moles of mn 1600 PBSA and 1 mole of ethyleneglycol salted with dimethyl ethanolamine. Emulsifier 2 was the emulsifier described in Examples 1-22, respectively. For Examples 23 and 24, Emulsifier 1 was the emulsifier described in Examples 23 and 24 respectively and Emulsifier 2 was the reaction product of hexadecenyl succinic anhydride/dimethylaminoethanol (1:1) mole.

Emulsion Preparation General Procedure

Solution 1

2-ethyl hexyl nitrate, 0.36 wt%
Emulsifier 1, 0.84 active wt%
Emulsifier 2, 0.31 active wt%
Diesel fuel 96.0-98.5 wt. %

Solution 2

Ammonium nitrate; 1.2 wt%
Distilled water, 98.8 wt%

In a Waring blender, about 80g of Solution 1 and about 20g of Solution 2 were combined and blended at low speed for about 5 minutes. Alternately, about 86.65g of Solution 1 and about 13.35 of Solution 2 were combined in the Waring Blender at high speed for about 6 minutes.

5 Using either procedure, the emulsions were decanted into a beaker, cooled to room temperature, and then transferred to about 130 ml oil solubility tubes for storage.

The water-blended fuels were rated by the following characteristics:

% oil: indicates height of clear diesel fuel at top of emulsion in storage bottle;

% oily emulsion: indicates height of fuel-rich emulsion below oil layer in emulsion;

10 % white/creamy emulsion: indicates height of target emulsion in storage bottle;

% band: indicates height of water-rich emulsion near bottom of storage;

% water: indicates height of free water broken from emulsion at bottom of storage bottle.

15 The emulsifier generally should have a maximum amount of white emulsion and minimal amount of the other layers.

Example 1

P-dodecylphenol (derived from propylene tetramer, about 130g, 0.496 moles, 1 molar equivalent) is charged into about a 500ml wide-neck, round-bottomed flask, along with sufficient odorless kerosene (about 186g) to make about a 50 w/w % solution of polymer in kerosene at the end of the reaction. The flask is then attached to an apparatus including flange lid, overhead stirrer/paddle-PTFE gland agitation system, Eurotherm/thermocouple/mantle heating system, Dean and Stark trap and condenser. The apparatus is lagged with glass wool from the top of the mantle to the bottom of the condenser.

25 The ingredients are then vigorously stirred and heated to about 30°C. 1M tetrabutylammonium hydroxide in methanol (about 20.8ml 4.96×10^{-3} moles, 0.01 molar equivalents) is then added via a pressure-equalizing dropping funnel. The reaction mixture is then heated quickly to about 60°C and formalin (about 37% w/w formaldehyde in water, about 55g, about 0.678 moles, 1.35 molar equivalents) is added dropwise over 11 minutes, 30 taking care not to let the temperature rise above about 67°C. The solution became cloudy. On completion of addition, the solution was heated at about 60°C for about 90 minutes.

Oleylamine (about 55.7g, about 0.208 moles, 0.42 molar equivalents) was then added dropwise over about 5 minutes via a pressure equalizing dropping funnel. About a 25°C exotherm was noted. The solution became dark. Temperature is then increased as reflux allows, collecting and draining off water via the Dean and Stark trap, to an eventual
5 temperature of about 140°C. This takes about 100 minutes. The solution became clearer. A total of about 48ml of water was collected. Once no more water is collected, the solution is held with stirring at about 140°C for about 2.5 hours. After this time the solution is clear and dark brown. The solution is then allowed to cool and poured into storage containers.

The results are shown in Table I.

Example 2

The procedure and apparatus described for Example 1 above were used, with the following changes in ingredient amounts. The tetrabutylammonium hydroxide was replaced with potassium hydroxide (about 0.28g, about 4.96×10^{-3} moles, 0.01 molar equivalents), the
15 kerosene amount was altered to about 103g, thus giving a 60% solution of polymer, and the oleylamine was replaced with ethylene diamine (about 25.0g, 0.417 moles, 0.84 molar equivalents).

The results are shown in Table I.

Example 3

The procedure and apparatus described for Example 1 above were used, with the following changes in ingredient amounts. The kerosene amount was altered to about 103g, thus giving a 60% solution of polymer, and the oleylamine was replaced with ethylene
25 diamine (about 25.0g, 0.417 moles, 0.84 molar equivalents).

The results are shown in Table I.

Example 4

The procedure and apparatus described for Example 2 above were used, except the ethylene diamine amount was altered to about 12.5g (0.208 moles, 0.42 molar equivalents).

The results are shown in Table I.

Example 5

The procedure and apparatus described for Example 3 above were used, except the ethylene diamine amount was altered to about 12.5g (0.208 moles, 0.42 molar equivalents).

The results are shown in Table I.

Example 6

The procedure and apparatus described for Example 4 above were used, except the kerosene amount was altered to about 70g, thus giving about a 69% solution of polymer.

The results are shown in Table I.

Example 7

The procedure and apparatus described for Example 5 above were used, except the kerosene amount was altered to about 70g, thus giving about a 69% solution of polymer.

The results are shown in Table I.

Example 8

The procedure and apparatus described for Example 1 above was used, with the following changes in ingredient amounts. The kerosene amount was altered to about 70g, thus giving about a 69% solution of polymer, and the oleylamine was replaced with ethanolamine (about 25.5g, 0.417 moles, 0.84 molar equivalents).

The results are shown in Table I.

Example 9

The procedure and apparatus described for Example 2 above were used, with the following changes in ingredient amounts. The kerosene amount was altered to about 76.5g, thus giving about a 67% solution of polymer, and the ethylene diamine was replaced with ethanolamine (about 25.5g, 0.417 moles, 0.84 molar equivalents).

The results are shown in Table I.

Example 10

The procedure and apparatus described for Example 1 above was used, with the following changes in ingredient amounts. The kerosene amount was altered to about 78g, thus giving about a 69% solution of polymer, and the oleylamine was replaced with diethanolamine (about 43.8g, 0.417 moles, 0.84 molar equivalents).

The results are shown in Table I.

Example 11

The procedure and apparatus described for Example 2 above were used, with the following changes in ingredient amounts. The kerosene amount was altered to about 78g, thus giving about a 69% solution of polymer, and the oleylamine was replaced with diethanolamine (about 43.8g, 0.417 moles, 0.84 molar equivalents).

The results are shown in Table I.

Example 12

The procedure and apparatus described for Example 11 above were used, except the diethanolamine amount was altered to about 21.8 g (0.208 moles, 0.42 molar equivalents) and the kerosene to about 68g, thus maintaining about a 69% solution of polymer.

The results are shown in Table I.

Example 13

The procedure and apparatus described for Example 11 above were used, except the diethanolamine amount was altered to about 67.3g (0.64 moles, 1.29 molar equivalents) and the kerosene to about 89g, thus maintaining about a 69% solution of polymer.

The results are shown in Table I.

Example 14

The procedure and apparatus described for Example 8 above were used, except the diethanolamine amount was altered to about 21.8g (0.208 moles, 0.42 molar equivalents) and the kerosene to about 68g, thus maintaining about a 69% solution of polymer.

The results are shown in Table I.

Example 15

The procedure and apparatus described for Example 8 above were used, except the diethanolamine amount was altered to about 67.3g (0.64 moles, 1.29 molar equivalents) and the kerosene to about 89g, thus maintaining about a 69% solution of polymer.

The results are shown in Table I.

Example 16

P-dodecylphenol (derived from propylene tetramer, about 130g, 0.496 moles, 1 molar equivalent) is charged into about a 500ml wide-neck, round-bottomed flask, along with sufficient Solvesso 150 (Ex Exxon) (about 100.35g) to make an about 60 w/w % solution of actives in Solvesso 150 at the end of the reaction. The flask is then attached to an apparatus including flange lid, overhead stirrer/paddle/PTFE gland agitation system, Eurotherm/thermocouple/mantle heating system, Dean and Stark trap and condenser. The apparatus is lagged with glass wool from the top of the mantle to the bottom of the condenser.

The ingredients are then vigorously stirred and heated to about 30°C. P-toluenesulphonic acid (about 0.95g, 4.96×10^{-3} moles, 0.01 molar equivalents) is then added. The reaction mixture is then heated quickly to about 60°C and formalin (about 37% w/w formaldehyde in water, about 32.5g, 0.397 moles, 0.8 molar equivalents) is added dropwise over about 11 minutes, taking care not to let the temperature rise above about 67°C. The solution became cloudy. On completion of addition, the solution was heated at about 60°C for about 300 minutes. Ethylene diamine (about 6.0g, 0.099 moles, 0.2 molar equivalents) and more formalin (about 37% w/w formaldehyde in water, 9.12g, 0.112 moles, 0.225 molar equivalents) were then added dropwise over 5 minutes via a pressure-equalizing dropping funnel. Temperature is then increased to an eventual temperature of about 140°C as refluxed and the water is collected and drained via the Dean and Stark trap. This takes about 100 minutes. The solution became much clearer. A total of about 48ml of water was collected. Once no more water is collected, the solution is held with stirring at about 140°C for about 2.5 hours. After this time the solution is clear and golden brown. The solution is then allowed to cool and poured into storage containers.

The results are shown in Table I.

Example 17

P-dodecylphenol (derived from propylene tetramer, about 130g, 0.496 moles, 1 molar equivalent) is charged into about a 500ml wide-neck, round-bottomed flask, along with sufficient Solvesso 150 (Ex Exxon) (about 100.35g) to make a about 60 w/w % solution of
5 actives in Solvesso 150 at the end of the reaction. The flask is then attached to an apparatus including flange lid, overhead stirrer/paddle/PTFE gland agitation system, Eurotherm/thermocouple/mantle heating system, Dean and Stark trap and condenser. The apparatus is lagged with glass wool from the top of the mantle to the bottom of the condenser. The ingredients are then vigorously stirred and heated to about 30°C. P-toluenesulphonic
10 acid (about 0.95g, 4.96×10^{-3} moles, 0.01 molar equivalents) is then added. The reaction mixture is then heated quickly to about 60°C and formalin (about 37% w/w formaldehyde in water, about 32.5g, 0.397 moles, 0.8 molar equivalents) is added dropwise over about 11 minutes, taking care not to let the temperature rise above about 67°C. The solution became cloudy. On completion of addition, the solution was heated at about 60°C for about 150
15 minutes. Ethylene diamine (about 6.0g, 0.099 moles, 0.2 molar equivalents) and more formalin (about 37% w/w formaldehyde in water, 9.12g, 0.112 moles, 0.225 molar equivalents) was then added dropwise over about 5 minutes via a pressure-equalizing dropping funnel. Temperature is then increased as reflux allows, collecting and draining off water via the Dean and Stark trap, to an eventual temperature of about 140°C. This takes
20 about 100 minutes. The solution usually becomes much clearer. A total of about 48ml of water was collected. Once no more water is collected, hold with stirring at about 140°C for about 2.5 hours. After this time the solution should be clear and golden brown. The solution is then allowed to cool and poured into storage containers.

The results are shown in Table I.

Example 18

The procedure and apparatus described for Example 17 were used except about 10.3g aminoethylethanolamine (0.099 moles, 0.2 molar equivalents) was used instead of ethylene
30 diamine and the kerosene amount altered to about 94g, thus maintaining about a 60% solution of polymer.

The results are shown in Table I.

Example 19

The procedure and apparatus described for Example 16 were used except about 10.4g diethanolamine (0.099 moles, 0.2 molar equivalents) was used instead of ethylene diamine and the kerosene amount altered to about 94g, thus maintaining about a 60% solution of polymer.

The results are shown in Table I.

Example 20

The procedure and apparatus described for Example 17 were used except about 10.4g diethanolamine (0.099 moles, 0.2 molar equivalents) was used instead of ethylene diamine and the kerosene amount altered to about 94g, thus maintaining a about 60% solution of polymer.

The results are shown in Table I.

Example 21

The procedure and apparatus described for Example 19 were used except the diethanolamine amount was altered to about 20.8g (0.2 moles, 0.4 molar equivalents) and the kerosene amount altered to about 101g, thus maintaining about a 60% solution of polymer.

The results are shown in Table I.

Example 22

The procedure and apparatus described for Example 20 were used except the diethanolamine amount was altered to about 20.8g (0.2 moles, 0.4 molar equivalents) and the kerosene amount altered to about 101g, thus maintaining about a 60% solution of polymer.

The results are shown in Table I.

The results for Examples 1-22 are shown in the Table I below after 4 weeks of storage at about 20°C.

TABLE I

Eg. No.	R	R'	X	n	% Oil	% Oily	% Creamy/ White	% Band	% H ₂ O
1	H	Oleyl	H+CH ₂ OH	Avg. 3	0	3	96	1	0
2	H	CH ₂ NH ₂	CH ₂ NRR'	Avg. 7	0	1.5	98	0.5	0
3	H	CH ₂ NH ₂	CH ₂ NRR'	Avg. 3	0	1.5	98	0.5	0
4	H	CH ₂ NH ₂	H+CH ₂ OH	Avg. 7	0	1.5	98	0.5	0
5	H	CH ₂ NH ₂	H+CH ₂ OH	Avg. 3	0	1.5	98	0.5	0
6	H	CH ₂ NH ₂	H+CH ₂ OH	Avg. 7	0	1.5	98	0.5	0
7	H	CH ₂ NH ₂	H+CH ₂ OH	Avg. 3	0	1.5	98	0.5	0
8	H	CH ₂ CH ₂ OH	CH ₂ NRR'	Avg. 3	0	2	96	1	0
9	H	CH ₂ CH ₂ OH	CH ₂ NRR'	Avg. 7	0	2	97	1	0
10	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	CH ₂ NRR'	Avg. 3	0	1.5	98	0.5	0
11	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	CH ₂ NRR'	Avg. 7	0	2	97	1	0
12	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	H+CH ₂ OH	Avg. 7	0	2	97	1	0
13	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	CH ₂ NRR'*	Avg. 7	0	1	98	1	0
14	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	H+CH ₂ OH	Avg. 3	0.5	1	97.5	1	0
15	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	CH ₂ NRR'*	Avg. 3	0	2	97	1	0
16	H	CH ₂ NH ₂	H	Avg. >8	0	2	97	1	0
17	H	CH ₂ NH ₂	H	Avg. 8	1	1	97	1	0
18	CH ₂ CH ₂ OH	CH ₂ NH ₂	H	Avg. 8	0	2	97	1	0
19	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	H	Avg. >8	0	2	97	1	0
20	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	H	Avg. 8	1	1	97	1	0
21	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	CH ₂ NRR'	Avg. >8	1	1	97	1	0
22	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	CH ₂ NRR'	Avg. 8	1	1	97	1	0

All of the above materials were tested as water-blended fuel emulsifiers in the formulation shown in the emulsion screening section.

- 5 The above results demonstrate excellent emulsion stability and minimal separation of the fuel and water phases.

Example 1 demonstrates the use of an oleylamine and a low molecular weight Resole is a good emulsifier and makes a good emulsion.

- 10 Examples 2-7 demonstrate that using either a potassium hydroxide or an ammonium hydroxide catalyst to make a Resole and then reacting it with either high or low amounts of

ethylene diamine having a high or low concentration of polymer in the end product gives a good emulsion.

Examples 8 and 9 demonstrate that using an ethanolamine and a Resole made with potassium hydroxide or tetrabutyl ammonium hydroxide catalyst gives a good emulsion.

5 Examples 10-15 demonstrate that using a Resole made with potassium hydroxide or a diethanolamine at high or low levels gives good emulsions.

Examples 16 and 17 demonstrate that using either a high or very high molecular weight Novalak resin and ethylene diamine gives a good emulsion.

10 Example 18 demonstrates that aminoethylethanolamine and a Novalak resin gives a good emulsion.

Examples 19-22 demonstrate that using diethanolamine at high or low levels with high or very high molecular weight Novalak gives a good emulsion.

Example 23

15 A 500-ml flask was equipped with an overhead stirrer, a thermocouple, and a reflux condenser. The flask was charged with 1000 MW PIB phenol (121g, 0.10 mol) paraformaldehyde (6.43g, 0.195 mole) and isopropanol (20g). The mixture was heated to 65°C and a 50% aqueous sodium hydroxide solution (1.63g, 0.02 mol) was added over one minute. The mixture was heated to 75°C over 5 minutes, and was held at 75-77°C for 2 hours
20 (no visible solids remained). The mixture was heated for an additional 50 minutes, glacial acetic acid was added over 2-3 minutes, and the mixture stirred at 75°C for 5 minutes.

To the reaction mixture was charged diethanolamine (18.9g, 0.18 mol) and after 30 minutes at 75°C a Dean-Stark trap was placed between the flask and condenser and the mixture was heated to 117°C over 1 hour, 40 minutes, over which time distillate collected in
25 the Dean-Stark trap. The mixture was then heated to 133°C over 20 minutes and N₂ gas was blown above the surface of the mixture at the rate of 0.1 standard cubic feet per hour (scfh). The mixture was heated to 150°C over 55 minutes, held at that temperature for 30 minutes and diluent oil (94.8g) was added to yield the product. The results in emulsification screening
30 demonstrate the use of a PIB-substituted amino phenol as an emulsifier provides good stability for a water emulsified fuel.

Example 24

Reaction Product of 1000MW PIB phenol/formaldehyde/diethanolamine (1:1:2.1)m

A 500-ml flask equipped with an overhead stirrer, thermocouple, Dean-Stark trap, and above surface N₂ inlet was charged with 1000 MW PIB phenol (121g, 0.10 mol), diluent oil (90g) and isopropanol (19g). The mixture was heated to 65°C and diethanolamine (11.55g, 0.11 mol) was added rapidly, stirred for 5 minutes, and a 37% aqueous solution of formaldehyde (9.72g, 0.12 mol) was added in one portion. The mixture was heated to 90°C over 50 minutes, held at that temperature for 30 minutes, and heated to 100°C for 30 minutes (17g of distillate collected in the trap). The mixture was heated to 115°C over 25 minutes, additional distillate was collected (5g), and the reaction mixture became clear. The mixture was then heated to 150°C over 15 minutes, held at that temperature for 1 hour, 20 minutes, and the resulting material was cooled and bottled as the product. The results in emulsification screening demonstrate the use of a PIB-substituted amino phenol as an emulsifier provides good stability for a water emulsified fuel.